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Characterization of Kerosene Heater Emissions Inside
Two Mobile Homes

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CHARACTERIZATION OF KEROSENE HEATER EMISSIONS INSIDE TWO MOBILE HOMES

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In an effort to determine the impact of kerosene heater emissions on indoor air quality, measurements were made in and around two mobile homes at a rural mobile home park near Apex, NC. The sampling was performed at two single-wide mobile homes equipped with kerosene heaters. The concentrations of acidic aerosols and gases, fine and coarse particulate aerosol mass, carbon monoxide, nitrogen oxides, volatile organic compounds, and semivolatiles, were determined for periods of heater operation and for periods in which heaters were not operated. Simultaneous outdoor measurements of acid aerosols and gases, fine and coarse aerosol mass, and volatile organic compounds were conducted to determine the contribution of outdoor pollutants to the indoor concentrations. Comparisons between the concentrations obtained from the analysis of outdoor, heater-on, and heater-off samples allowed us to examine the impacts of the kerosene emissions on indoor concentrations. Concentrations of sulfates, aerosol strong acidity, fine and coarse aerosol mass, carbon monoxide, and sulfur dioxide were found to be higher when the heater was operated; however, these heater-on concentrations were comparable to those observed in moderately polluted atmospheres. Indoor concentrations of nitrous acid and nitrogen oxides during heater operation were found to be considerably higher than those observed in polluted atmospheres. Finally, use of kerosene heaters was found to be responsible for increased concentrations of non-methane volatile and semi-volatile organic compounds indoors. Acid aerosol indoor concentrations were quite variable during the study and were found to exist in the presence of excess ammonia.

INTRODUCTION

Elevated indoor concentrations of pollutants have been measured inside homes with combustion sources such as gas stoves^{1,2} and wood burners or fireplaces.^{3,4} Also, preliminary studies have suggested that kerosene heaters can emit considerable amounts of nitrogen oxides, sulfur dioxide, carbon monoxide, and acid aerosols⁵ and mutagenic organic compounds.⁶ Furthermore, recent studies have demonstrated that the primary pollutants emitted from the indoor combustion sources can react on indoor surfaces to produce secondary pollutants. For instance, high concentrations of nitrous acid have been found to be associated with heterogeneous processes.^{7,8} The main objective of this study is to enhance our understanding of human exposures to the broad spectrum of indoor air pollutants, such as acidic aerosols and gases as well as volatile and semi-volatile organic compounds, emitted from kerosene heaters.

SAMPLING AND ANALYSIS

The sampling was performed at two single-wide (14' x 52' and 14' x 76') mobile homes located in a rural mobile home park. No industrial, automotive, or other air pollutant emission sources were near the study site. Home A was equipped with a 6,800 BTU Radiant (Koehring KRB-68) heater, and home B was equipped with a 20,000 BTU convective (Omni 1050 heater). Both the homes used electric heat pumps and electric stoves. There were no other indoor combustion sources besides the kerosene heaters. Outdoor monitoring was conducted at a single site in the mobile park. There were six sampling periods: three with the heater on and three with the heater off. Sampling was conducted simultaneously in both homes and outdoors. For both heater-on and heater-off periods, sampling started at 4 p.m. each day and concluded at approximately 11 p.m. For periods of heater operation, the heaters were on from 4 pm until approximately 9 p.m. Sampling continued until 11 p.m. to collect most of the slowly decaying pollutants in the two homes. The central air system, coupled with the electric heat pump, was not used while the kerosene heater was in operation.

An annular denuder/filter pack system was used to collect nitric acid, sulfur dioxide, nitrous acid, and ammonia gases and particle acidity, sulfate, nitrate, and ammonium concentrations;^{9,10} PM₁₀ particulate mass samples were collected on a 75 mm Teflon-coated glass fiber filter using an Andersen sampler. Fine aerosol, ≤ 2.1 microns, were collected using a glass impactor. Nonmethane organic compounds (NMOC) were collected into an evacuated canister; C-2 to C-12 hydrocarbons were determined by capillary gas chromatography with flame ionization detection and cryogenic sample pre-concentration.¹¹ In addition, semi-volatile organic compounds (SVOC) were sampled using a 65 gram XAD-2 trap collecting directly downstream of the Pallflex Teflon-coated glass fiber filter of the Andersen PM₁₀ sampler. The collected SVOC were recovered from XAD-2 resin by Soxhlet extraction with dichloromethane. Organics having a boiling point greater than 300°C were determined initially; subsequently, the extracts were analyzed for total chromatographable organics (compounds having a boiling point between 100° and 400°C). Continuous measurements of carbon monoxide were conducted in both mobile homes, using a General Electric portable SPE electrochemical detector. Also temperature and relative humidity were measured throughout the monitoring period with hygrothermographs. Nitrogen oxide concentrations were measured in home B using a chemiluminescence analyzer. Similar measurements were collected outdoors for acidic aerosols and gases, fine and PM₁₀ aerosol mass, and volatile organic compounds, using the same techniques as indoors. The mobile home air exchange rate was determined using the perfluorocarbon tracer technique.¹²

RESULTS AND DISCUSSION

Acid Aerosols and Gases

Table 1A depicts the aerosol strong acidity, expressed in nmoles/m³ of H⁺, for the outdoor site and mobile homes A and B. For indoor sites, two side-by-side annular denuder filter pack systems were used for sampling, whereas for outdoor sampling only one system was employed. Negative H⁺ concentrations reflect the presence of alkaline particles collected on the Teflon filter. Because the Teflon filter is extracted by a 10⁻⁴N perchloric acid aqueous solution, the presence of alkaline particles will increase the pH of the extraction solution resulting in the determination of negative H⁺ values. Although the acid aerosol concentrations were higher when the heater was on, they are still very low compared to those observed in relatively polluted atmospheres. The observed acidity levels, expressed in equivalent sulfuric acidity, vary between 1-3 $\mu\text{g}/\text{m}^3$. Table 1A also gives the particulate sulfate concentration for mobile homes A and B and outside, for heater on and off periods. Sulfate concentrations in mobile home B were approximately twice as high as in mobile home A. Mobile home B also presented higher particle acidity concentrations. If one considers that 70-90% of outdoor sulfates penetrate indoors,⁸ then, approximately 50% of the observed indoor levels in mobile home A can be attributed to kerosene heaters, while for mobile home B, the kerosene heater contribution is more than two thirds of the total sulfate concentrations.

Results shown in Table 1A indicate that for each home, sulfate levels were relatively stable for each "heater on" sampling period. Aerosol strong acidity, however, presented more variability between different sampling days. This variability cannot be explained by the differences in indoor ammonia concentrations, which changed very little throughout the study, as given by Table 1B. More importantly, indoors there was enough ammonia present to neutralize all acid aerosols. Neutralization processes of acid aerosols need to be investigated in order to improve our understanding of human exposures to these acidic pollutants. A summary of physio-chemical processes which may affect the ability of ammonia to diffuse into acidic aerosol sulfates has been previously presented.¹³ Thermodynamically, ammonia and acid aerosol cannot co-exist. However, the mobile home study data show they do exist together. Several hypotheses have been suggested and research is presently under way to help explain the phenomena.

Concentrations of nitrogen oxides, NO_x , were measured only in home B. For heater-off periods, NO concentrations were below the method of detection limits, 10 ppb for both pollutants, see Table 1B. For heater-on periods, average concentrations were significantly higher, with average concentrations of 296 ppb and 410 ppb for NO and NO_x , respectively. Note that the term NO_x includes nitrogen compounds such as NO , NO_2 , N_2O_3 , N_2O_4 , N_2O_5 , HNO_3 , or HONO . Concentrations of HNO_3 were very low, below the method detection limit, 5 ppb, as shown in Table 1B. In fact, a previous study⁸ suggests that indoor nitric acid concentrations are low due to the high deposition velocity. In contrast, concentrations of nitrous acid (HONO) represent a high percentage of total NO_x . Furthermore, Table 1B reveals that nitrous acid concentrations in home B vary between 30 and 40 ppb when the heater is on. Considerably lower levels, less than 10 ppb, were observed for the heater-off periods. For home A, concentrations were between 5 and 10 ppb for heater-on periods and less than 5 ppb for heater-off periods. Outdoor concentrations were below 1 ppb. Previous studies have shown that nitrogen dioxide can be reduced on different interior home surfaces.^{7,8}

Concentrations of sulfur dioxide were considerably higher during heater-on periods. Average heater-on concentrations were 11.3 and 21.7 ppb for homes A and B, respectively. During heater-off periods, concentrations were below the minimum detection limit, 1 ppb. Outside sulfur dioxide concentrations were 1.7 and 4.4 for heater on and off periods, respectively. The above results are in good agreement with previous measurements that suggest very low indoor/outdoor sulfur dioxide ratios for homes with no combustion sources. As in the case of nitric acid, sulfur dioxide presents higher deposition rates in the indoor environment due to its reactivity. Carbon monoxide concentrations were found to be two to four times higher for heater-on periods. Finally, the results of Table 1A show that fine particle concentrations were two to five times higher for heater-on periods, while for coarse particles, the heater-on average concentration was higher only for home B and lower for home A. Most of the coarse particles are associated with re-suspension of dust, vacuuming, or frying;¹⁴ thus, the coarse particle levels are expected to be dependent on different indoor activities, rather than combustion sources such as kerosene heaters.

A summary of the hydrocarbon results is shown in Table 2. Total, volatile non-methane organic compounds (NMOC), the sum of the C-2 to C-12 hydrocarbons, were an order of magnitude higher inside the mobile homes compared to the ambient air, when the kerosene heater was off as well as on. Direct volatilization of kerosene fuel when the heater is off may also contribute to high background hydrocarbon concentrations. The high NMOC background when the stoves were off suggests that hydrocarbons are adsorbing and desorbing from surfaces in the mobile homes. The NMOC emission rates from the stoves along with variable air exchange rates and stove settings yielded predictably high variable hydrocarbon concentrations as evidenced by the relatively high NMOC standard deviations shown in Table 2. Also, the total number of chromatographic peaks show the same trend (heater on > heater off > outdoor air), as the NMOC results.

Finally, Table 1C gives the concentrations of semivolatiles for homes A and B during the heater on and off periods. It shows the average concentrations of gravimetrics (boiling point $<300^{\circ}\text{C}$) and TCOs (boiling point $<400^{\circ}\text{C}$) for both homes. For home A, both gravimetric and TCO concentrations were considerably higher for heater-on periods, while for home B, concentration levels were similar for heater on and off periods. High background concentrations of semivolatiles can be related to the presence of other sources as well as to the direct volatilization of kerosene fuel when the heater is off. The mg/m^3 concentrations are a magnitude above normally polluted indoor atmospheres. Kerosene evaporations from the heaters in both the off and on modes is highly suspected.

CONCLUSIONS

Indoor concentrations of nitrous acid, nitrogen oxides, aerosol strong acidity, sulfate, fine aerosol mass, and carbon monoxide were found to be related to kerosene combustion. While concentrations of aerosol acidity, sulfate, fine and coarse aerosol mass, and carbon monoxide were moderately high, concentrations of nitrous acid and nitrogen oxides were up to 40 and 400 ppb, respectively. Furthermore, kerosene combustion emissions were found to result in an increase in concentrations of semivolatile and volatile organic compounds indoors.

Although our main objective was to characterize the emissions from kerosene heaters, the findings of this investigation underline the importance of different physico-chemical processes occurring in the indoor environment which can affect human exposures to pollutants originating from kerosene and other combustion sources. Future studies should examine the reduction mechanisms of nitrogen oxides on indoor surfaces resulting in the formation of nitrous acid. Also, it is possible that other secondary pollutants are formed through similar processes. Furthermore, the presence of acidic aerosols indoors, presumably coexisting with ammonia, suggests that the mechanisms of acid aerosol neutralization need further investigation. Although, in our study we examined a specific type of indoor combustion source, our findings are in good agreement with previous indoor studies conducted in homes with other types of combustion sources or homes with no sources. Modeling of human exposures to indoor pollutants will require not only the characterization of outdoor/indoor source emissions but also the assessment of physico-chemical processes affecting the transformation and fate of pollutants indoors. Reaction between ammonia and acid aerosol is not complete and could be influenced by factors that are not well understood at this time.

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Table 1. Data Summary for Indoor Heater Off and Heater On Conditions, Outdoor Conditions, and Air Exchange Rates

1A. Particulate Matter

Pollutant Measurements (observations = 3)	Average Concentrations					
	Home A		Home B		Outdoors	
	Heater Off	Heater On	Heater Off	Heater On	Off Period	On Period
H ⁺ (equivalent H ₂ SO ₄), µg/m ³	0.1 ± 0.009	0.7 ± 0.5	0.5 ± 0.3	2.2 ± 0.3	0.4 ± 0.2	0.2 ± 0.1
H ⁺ , nmoles/m ³	2.2 ± 0.2	15.2 ± 10.3	10.3 ± 6.8	43.9 ± 5.0	7.3 ± 3.4	3.4 ± 2.0
NH ₄ ⁺ , µg/m ³	0.4 ± 0.3	1.3 ± 0.07	0.5 ± 0.3	2.8 ± 0.2	ND	ND
NH ₄ ⁺ , nmoles/m ³	22.1 ± 14.2	71.3 ± 4.1	27.5 ± 14.8	158 ± 13.1		
SO ₄ ²⁻ , µg/m ³	0.6 ± 0.6	2.6 ± 0.2	0.7 ± 0.7	7.1 ± 2.5	1.9 ± 1.1	2.0 ± 0.54
SO ₄ ²⁻ , nmoles/m ³	6.4 ± 6.4	27.5 ± 2.6	6.9 ± 6.9	74.2 ± 26.0	19.8 ± 11.8	20.9 ± 5.7
NO ₃ ⁻ , µg/m ³	ND	ND	0.1 ± 0.05	0.3 ± 0.08	0.1 ± 0.09	0.2 ± 0.1
NO ₃ ⁻ , nmoles/m ³			2.0 ± 1.0	4.8 ± 1.2	2.3 ± 2.0	3.0 ± 1.5
PM _{2.5} , µg/m ³	22.2 ± 2.4*	41.1 ± 7.2	13.4 ± 3.2*	84.3 ± 26.8	16.2 ± 3.2	9.5 ± 0.4
PM ₁₀ , µg/m ³	152 ± 83.0	95.9 ± 9.7	48.4 ± 7.8	155 ± 14.8	7.5 ± 1.2	13.9 ± 2.1

* = 2 Observations
ND = Nondetectable.

1B. Gases

Pollutant Measurements (observations = 3)	Average Concentrations					
	Home A		Home B		Outdoors	
	Heater Off	Heater On	Heater Off	Heater On	Off Period	On Period
HONO, ppb	0.8 ± 0.4	7.5 ± 0.7	6.9 ± 1.5	33.0 ± 1.1	0.4 ± 0.4	ND
HNO ₂ , ppb	ND	ND	ND	ND	ND	ND
SO ₂ , ppb	ND	11.3 ± 0.4	0.4 ± 0.3	21.7 ± 0.5	4.4 ± 2.2	1.7 ± 0.6
NH ₃ , ppb	19.4 ± 3.6	23.2 ± 2.0	38.4 ± 4.0	36.1 ± 3.0	1.4 ± 0.5	1.3 ± 0.3
CO, ppb	5.0	12.0	1.0	4.0	n/a	n/a
NO, ppb	n/a	n/a	ND	296 ± 64.0	n/a	n/a
NO ₂ , ppb	n/a	n/a	ND	114 ± 5.7	n/a	n/a
NMHC, ppm	1.9*	2.3 ± 0.4	3.4 ± 1.0	3.5 ± 0.8	0.14 ± 0.002*	

* = 1 Observation
* = Composite mean for On and Off periods, 2 observations.
ND = Nondetectable.
n/a = Not measured.

1C. Semivolatiles

Pollutant Measurements (observations = 3)	Average Concentrations					
	Home A		Home B		Outdoors	
	Heater Off	Heater On	Heater Off	Heater On	Off Period	On Period
Gravimetrics, mg/m ³ (B.P. < 300 °C)	0.26 ± 0.07*	0.88 ± 0.31	1.23 ± 0.3*	1.33 ± 0.2	n/a	n/a
TCO's, mg/m ³ (B.P. 100 - 400 °C)	0.84 ± 0*	3.0 ± 0.8	5.1 ± 0.06*	4.3 ± 0.7	n/a	n/a

* = 2 Observations
n/a = Not measured.

1D. Physical Parameters

Parameter (observations = 3)	Average Concentrations					
	Home A		Home B		Outdoors	
	Heater Off	Heater On	Heater Off	Heater On	Off Period	On Period
Air Exchange (exch/hr)	0.28 ± 0.06	0.19 ± 0.01	0.39 ± 0.02	0.62 ± 0.07	n/a	n/a
Temperature (°F)	55 ± 4.8	53 ± 1.2	75 ± 0.9	69 ± 4.8	48 ± 7.5	40 ± 1.2
Relative Humidity (%)	54 ± 0	48.5 ± 4.2	70 ± 4.7	57 ± 1.5	89 ± 1.4	81 ± 1.1

Table 2. Comparison of NMOC Concentrations in PPM as Carbon and Number of Chromatographic Peaks for Two Mobile Homes with Kerosene Heaters On and Off and Outdoor Air

Site/Heater Mode	NMOC, ppm				No. of Peaks
	n	mean	std.dev.	range	mean
Mobile Home A, Heater on	3	3.35	1.78	3.54	181
Mobile Home B, Heater on	3	3.50	1.40	2.80	224
Mobile Homes A & B, Heater off	4	2.24	0.61	1.41	167
Outdoor Air	2	0.14	0.003	0.004	137